Supporting Information for

A highly efficient Ga/ZSM-5 catalyst prepared by formic acid impregnation and *in-situ* treatment for propane aromatization

He Xiao,[a,b] Junfeng Zhang,[a] Xiaoxing Wang,[a] Qingde Zhang,[a] Hongjuan Xie,[a] Yizhuo Han,[a] and Yisheng Tan *[a]

a. State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China;

b. University of Chinese Academy of Sciences, Beijing 100049, China

***Correspondence to: Yisheng Tan Prof**. E-mail: tan@sxicc.ac.cn. Tel:+86-351-4044287. Fax:+86-351-4044287

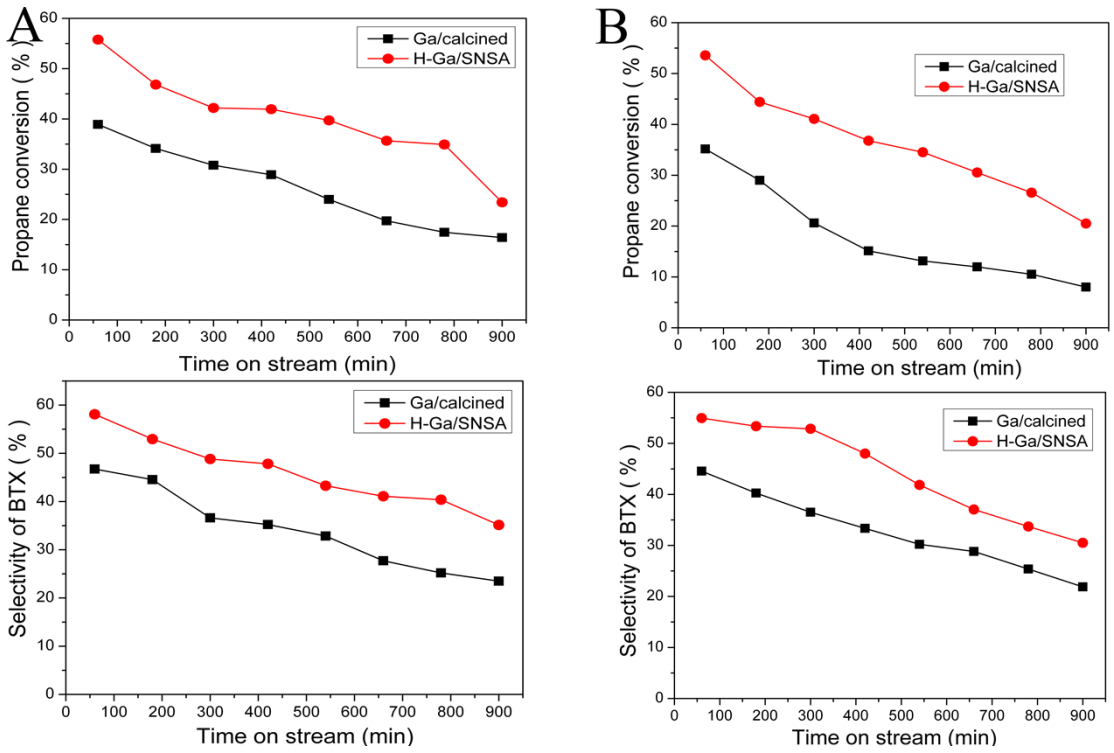

Fig. S1 Propane conversion (**A**) and selectivity of BTX (**B**) as a function of time on stream for Ga/calcined and H-Ga/SNSA. Reaction conditions: P = 100 kPa, T = 540 °C, WHSV = 6000 ml/(g·h) and N_2/C_3H_8 molar ratio = 2.

The stability of H-Ga/SNSA catalyst is investigated in comparison with that of Ga/calcined during two cycles of 900 min time-on-stream shown in Fig. S1. As observed, propane conversion and selectivity of BTX over Ga/calcined are 38.9% and 46.7% at the initial stage of reaction. And the Ga/calcined exhibits gradual deactivation pattern as a function of time on stream. After 900 min, propane conversion and selectivity of BTX over Ga/calcined decrease to 16.3% and 23.4% respectively. While propane conversion (55.7%) and selectivity of BTX (58.1%) over H-Ga/SNSA are superior to those over Ga/calcined respectively, at the initial stage of reaction. Gradual deactivation pattern as a function of time on stream is also exhibited for H-Ga/SNSA. Propane conversion and selectivity of BTX over H-Ga/SNSA are

higher than that on Ga/calcined during the whole test period. It's obvious that deactivation performance easily occurs over H-Ga/SNSA and Ga/calcined because of rapid coke deposition under the conditions of large space velocity. Besides, activities of these catalysts are investigated after regeneration through a thermo-treatment to remove coke deposition at 540 °C in air (Fig.S1B). It can be seen that activities of H-Ga/SNSA and Ga/calcined can be recovered substantially. Meanwhile, stability patterns of H-Ga/SNSA and Ga/calcined are similar to that before regeneration as a function of time on stream. Furthermore, the propane conversion and selectivity of BTX over H-Ga/SNSA are still higher than those on Ga/calcined for the whole reaction time. The results revealed that H-Ga/SNSA and Ga/calcined both show analogous stability behavior under large space velocity conditions as a function of time on stream, but H-Ga/SNSA prepared using our proposed novel method shows better catalytic performance than Ga/calcined prepared using conventional impregnation method always during the whole test period. In addition, activities of H-Ga/SNSA and Ga/calcined could recover after regeneration, and the H-Ga/SNSA still shows super catalytic performance in comparison with Ga/calcined. The results of the durability and regeneration tests suggest that the catalyst crystals are reasonably stable under the conditions of the aromatization reaction. Although the H-Ga/SNSA does not exhibit the super stability like the way we imagined, H-Ga/SNSA shows super catalytic performance in comparison with Ga/calcined during the whole test period.

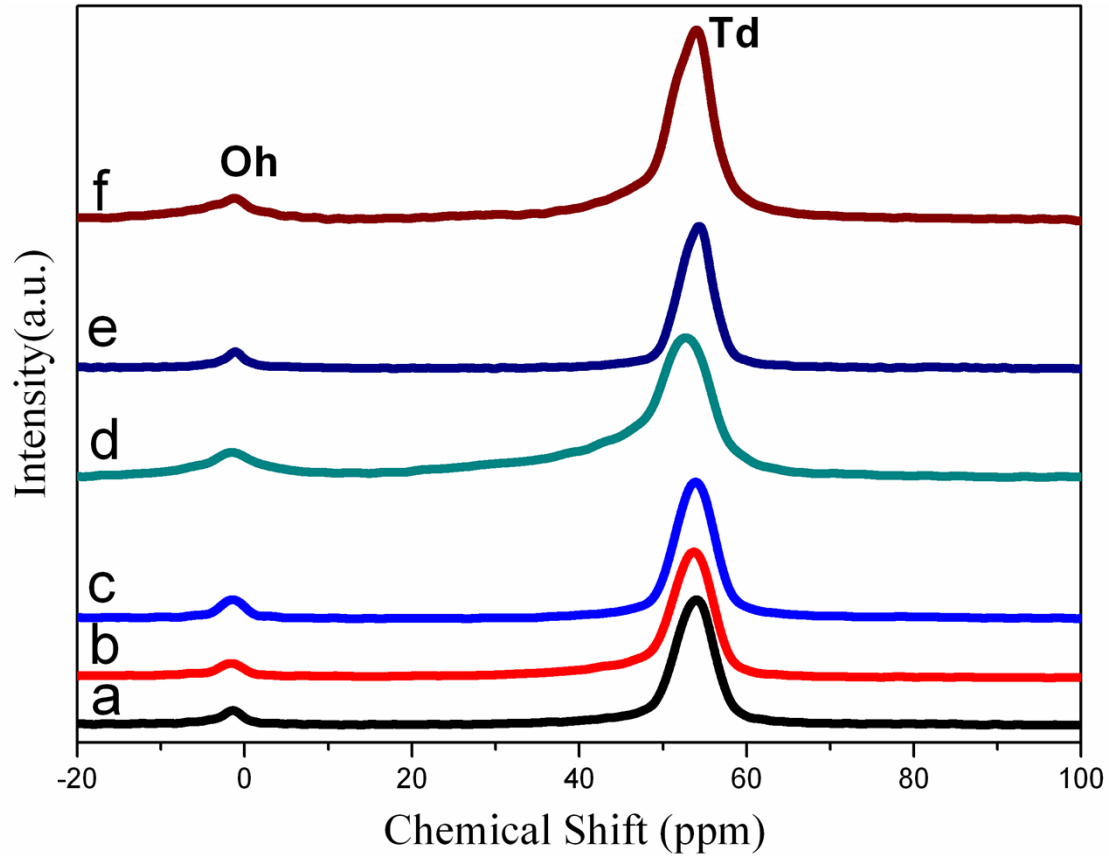

Fig. S2 ^{27}Al MAS NMR spectra of as-prepared ZSM-5 zeolites, showing four-coordinate framework Al peak (Td) and octahedral extra framework Al peak (Oh). (a) HZSM-5; (b) Ga/calcined; (c) Ga/dried;(d) Ga/SNSA; (e) H-Ga/dried; (f) H-Ga/SNSA

Fig. S3 TG-MS profile of H-Ga/dried, showing water steam generated by self-decomposition of Ga species and other species during *in-situ* treatment process.

Table S1 Summary of H_2-TPR results of percentage composition for as-prepared samples. This table suggests the percentage compositions of $(GaO)^+$ on H-Ga/SNSA is higher than that on other catalysts.

Samples	small Ga_2O_3 particles (%)	$(GaO)^+$ species (%)	segregated bulk Ga_2O_3 (%)
Ga_2O_3	507(93.8)	/	771(6.18)
Ga/calcined	528(94.2)	671(2.40)	810(3.28)
Ga/SNSA	533(69.8)	648(28.9)	839(1.30)
H-Ga/SNSA	532(62.3)	650(37.3)	822(0.360)